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(54) Titre : SOLUTIONS AQUEUSES OU DISPERSIONS D'OLIGOURETHANES CONTENANT DES GROUPEMENTS (METH)ACRYLOYL, PROCEDE DE PRODUCTION ET SUBSTRATS ENDUITS QUI EN DERIVENT

(54) Title: AQUEOUS SOLUTIONS OR DISPERSIONS OF OLIGOURETHANES CONTAINING (METH)ACRYLOYL GROUPS, A PROCESS FOR THEIR PRODUCTION AND COATED SUBSTRATES PREPARED THEREFROM

(57) Abrégé/Abstract:

The present invention relates to aqueous solutions or dispersions of oligourethanes having a pH of 6.0 to 8.5 wherein the dissolved or dispersed oligourethanes contain carboxyl groups at least partially neutralized with ammonia and have i) a double bond content in the form of (meth)acryloyl groups (expressed as C=C, molecular weight 24) of 3 to 15% by weight and ii) a content of carboxyl groups, including the carboxyl groups neutralized with ammonia, which corresponds to an acid value of 20 to 100. The present invention also relates to a process for the preparation of these aqueous solutions or dispersions of oligourethanes and to their use for the preparation of coated substrates.

AQUEOUS SOLUTIONS OR DISPERSIONS OF OLIGOURETHANES
CONTAINING (METH)ACRYLOYL GROUPS, A PROCESS FOR
THEIR PRODUCTION AND COATED SUBSTRATES PREPARED THEREFROM

ABSTRACT OF THE DISCLOSURE

The present invention relates to aqueous solutions or dispersions of oligourethanes having a pH of 6.0 to 8.5 wherein the dissolved or dispersed oligourethanes contain carboxyl groups at least partially neutralized with ammonia and have

- i) a double bond content in the form of (meth)acryloyl groups (expressed as C=C, molecular weight 24) of 3 to 15% by weight and
- ii) a content of carboxyl groups, including the carboxyl groups neutralized with ammonia, which corresponds to an acid value of 20 to 100.

The present invention also relates to a process for the preparation of these aqueous solutions or dispersions of oligourethanes and to their use for the preparation of coated substrates.

AQUEOUS SOLUTIONS OR DISPERSIONS OF OLIGOURETHANES
CONTAINING (METH)ACRYLOYL GROUPS, A PROCESS FOR
THEIR PRODUCTION AND COATED SUBSTRATES PREPARED THEREFROM

BACKGROUND OF THE INVENTION

5 Field of the Invention

 This invention relates to aqueous solutions or
dispersions of certain ionically modified oligourethanes
containing (meth)acryloyl groups, to a process for their
production and to coated substrates prepared therefrom.

10 Description of the Prior Art

 Polyurethanes containing (meth)acryloyl groups
(so-called urethane (meth)acrylates) have long been known and
are eminently suitable as binders, for example for paints (cf.
for example DE-OS 2,737,406). The relatively high viscosity of
15 these products almost always necessitates the use of organic
solvents.

 Water-dilutable urethane (meth)acrylates are also
known (cf. for example, DE-OS 2,936,039). The hydrophilicity
of these known systems is based on the presence of ionic
20 centers, particularly sulfonate groups, which contain as
counterions alkali cations or ammonium ions (from tertiary
amines) which at least partly remain in the coatings ultimately
obtained from the systems and considerably impair their water
resistance.

25 Accordingly, an object of the present invention is to
provide new aqueous solutions or dispersions of urethane
(meth)acrylates which are stable in storage without the
addition of dispersants or external emulsifiers, without alkali
cations and without ammonium ions from tertiary amines, and
30 which may be cured to form coatings combining resistance to
water and chemicals with favorable mechanical properties.

This object may be achieved in accordance with the solutions or dispersions of the present invention which are described in detail hereinafter and by the process for their production. The principal feature of the invention is that
5 carboxyl groups at least partly neutralized with ammonia are incorporated into the urethane (meth)acrylates using 2,2-bis-(hydroxymethyl)-alkane carboxylic acids.

DE-OS 3,641,494 relates to a process in which polyurethane elastomers dispersible in water are modified with
10 anions. Nevertheless, it can be said that the solution provided by the present invention to the stated object was not obvious from this prior publication. The solutions or dispersions of oligourethanes according to the present invention, which are described in detail hereinafter, differ
15 from the solutions or dispersions of polyurethanes according to the reference in several areas:

- The polyurethanes according to the prior publication are polyurethane elastomers wherein the molecules are based on structural units attributable to the incorporation of
20 relatively high molecular weight compounds containing at least two isocyanate-reactive groups, particularly hydroxyl groups. The oligourethanes according to the invention contain no such structural units.
- The polyurethanes according to the prior publication
25 contain terminal or lateral polyether chains containing ethylene oxide units as further hydrophilic centers which are not present in the oligourethanes according to the invention.
- In addition to the ammonium carboxylate groups, the
30 oligourethanes according to the present invention also have a high concentration of (meth)acryloyl groups, which is not the case with the polyurethanes according to the prior publication. It could not have been expected that it would be possible to produce storable aqueous solutions
35 or dispersions of oligourethanes containing both high

concentrations of (meth)acryloyl groups and ammonia in the form of ammonium groups because it is known that ammonia, in the same way as primary or secondary amines, reacts spontaneously with activated double bonds by Michael addition. Accordingly, it could not have expected that the principle of ionic modification according to DE-OS 3,641,494 would be applicable to oligourethanes containing (meth)acryloyl groups of the type present in the solutions or dispersions according to the present invention.

SUMMARY OF THE INVENTION

The present invention relates to aqueous solutions or dispersions of oligourethanes having a pH of 6.0 to 8.5 wherein the dissolved or dispersed oligourethanes contain carboxyl groups at least partially neutralized with ammonia and have

- i) a double bond content in the form of (meth)acryloyl groups (expressed as C=C, molecular weight 24) of 3 to 15% by weight and
- ii) a content of carboxyl groups, including the carboxyl groups neutralized with ammonia, which corresponds to an acid value of 20 to 100.

The present invention also relates to a process for the preparation of aqueous solutions or dispersions of oligourethanes by reacting

- a) 20 to 80% by weight of an alcohol component containing at least one monohydric alcohol having one or more (meth)acryloyl groups and a molecular weight of 116 to 1,000,
 - b) 4.5 to 20% by weight of at least one 2,2-bis-(hydroxymethyl)-alkane carboxylic acid having at least 5 carbon atoms and
 - c) 15 to 75% by weight of at least one polyisocyanate component containing at least one organic polyisocyanate having a molecular weight of 168 to 1,000,
- by initially introducing components a) and b), then reacting these components with component c) at a temperature of 50 to

100°C until the reaction mixture contains no more free isocyanate groups and subsequently dissolving or dispersing the reaction mixture in water, the carboxyl groups being at least partly neutralized by addition of ammonia during the dissolving or dispersing step so that the resulting solution or dispersion has a pH value of 6.0 to 8.5, wherein

- A) the percentages of a), b) and c) add up to 100, based on the weight of a), b) and c),
- B) the amounts of a), b) and c) correspond to an NCO:OH equivalent ratio of 0.5:1 to 1:1 and
- C) the amounts of a), b) and c) are otherwise selected within the stated limits so that the resulting oligourethanes have
 - i) a double bond content in the form of (meth)acryloyl groups (expressed as C=C, molecular weight 24) of 3 to 15% by weight and
 - ii) a content of carboxyl groups, including the carboxyl groups neutralized with ammonia, which corresponds to an acid value for the oligourethanes of 20 to 100.

Finally, the present invention is directed to coated substrates prepared from these solutions or dispersions of oligourethanes.

DETAILED DESCRIPTION OF THE INVENTION

Component a) contains at least one monohydric alcohol containing one or more (meth)acryloyl groups. Examples include esters which contain on average one free hydroxyl group and which are prepared from acrylic acid or methacrylic acid and polyhydric alcohols. The esters have a molecular weight of 116 to 1,000, preferably 116 to 750. Examples of such ethylenically unsaturated esters are hydroxyethyl (meth)acrylate, 2- and 3-hydroxypropyl (meth)acrylate, 2-, 3- and 4-hydroxybutyl (meth)acrylate and reaction products of trimethylol propane or alkoxylated trimethylol propane with (meth)acrylic acid, such as the reaction product of 2 moles of acrylic acid with 1 mole

-5-

of an ethoxylated trimethylol propane (OH value 550, degree of ethoxylation approx. 4).

Component b) contains at least one 2,2-bis-(hydroxymethyl)-alkane carboxylic acid having at least 5 carbon atoms, preferably 2,2-bis-(hydroxymethyl)-propionic acid.

Component c) contains at least one organic polyisocyanate. Suitable polyisocyanates include any organic polyisocyanate known from polyurethane chemistry having aliphatically, cycloaliphatically and/or aromatically bound isocyanate groups and a molecular weight of 168 to 1,000, preferably 168 to 300. Examples of suitable polyisocyanates include 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (IPDI); 4,4'-diisocyanatodicyclohexyl methane; 4,4'-diisocyanatodiphenyl methane and mixtures thereof with 2,4'-diisocyanatodiphenyl methane and, optionally, the higher homologs of these diisocyanates; and 2,4-diisocyanatotoluene and mixtures thereof with 2,6-diisocyanatotoluene.

Biuret-, isocyanurate- or urethane-modified polyisocyanates based on these monomeric polyisocyanates are also suitable. These derivatives generally have a molecular weight less than 1,000. The preparation of these derivatives is described, for example, in U.S. Patents 3,124,604, 3,183,112, 3,919,218 and 4,324,879.

The oligourethanes present in the solutions or dispersions according to the invention have the above-mentioned content of olefinic double bonds. This content is preferably between 4 and 10% by weight. The oligourethanes have an acid value of 20 to 100, preferably 25 to 80 mg KOH/g; the acid value encompasses both the free carboxyl groups and also the carboxyl groups neutralized with ammonia. At least some, preferably 45 to 100% and more preferably 60 to 100%, of the carboxyl groups are neutralized with ammonia, i.e., are present as carboxylate groups. At the same time, it is important during neutralization of the carboxyl groups to ensure that the pH value of the aqueous solutions or dispersions is between 6.0

Mo-3552

and 8.5, preferably between 6.5 and 8.0. The solutions or dispersions according to the invention generally have a solids content of 30 to 55% by weight, preferably 35 to 50% by weight.

5 The oligourethanes according to the invention are reaction products of comparatively low molecular weight starting materials in the presence of large quantities of chain-terminating synthesis components. Accordingly, there is every justification to refer to these reaction products not as "polyurethanes," but instead as "oligourethanes" which have an average molecular weight calculated from the stoichiometry of the starting materials of 700 to 5,000, preferably 700 to 2,000.

15 In the practical application of the process according to the invention, component a) is preferably used in a quantity of 25 to 75% by weight, component b) is preferably used in a quantity of 5 to 19% by weight and component c) is preferably used in a quantity of 20 to 70% by weight, the percentages of a), b) and c) adding up to 100, based on the weight of a), b) and c). In addition, it is important in accordance with the present invention to ensure that the starting components are used within the stated limits so that an NCO:OH equivalent ratio of 0.5:1 to 1:1, preferably 0.7:1 to 1:1 is maintained. The polyisocyanate c) is generally used in slightly less than the stoichiometric quantity so that the end of the reaction is reached when no more isocyanate groups can be detected in the reaction mixture. Finally, the reactants and their amounts are suitable selected within the stated limits to ensure that the oligourethanes have the required double bond content and acid number.

25 The reaction according to the invention is preferably carried out in the presence of inert solvents at solids contents of 60 to 95% by weight. Suitable solvents include dimethyl diglycol, N-methyl pyrrolidone, N-methyl caprolactone, ethyl glycol acetate, n-butyl acetate, acetone and mixtures of these solvents.

30 Mo-3552

To carry out the reaction, the alcohol component a) containing the (meth)acryloyl groups, the 2,2-bis-(hydroxy-methyl)-alkane carboxylic acid b) and the solvent preferably used are homogenized, the polyisocyanate c) is added over a
5 period of 1 minute to 2 hours at 50 to 100°C and the reaction mixture is then stirred at 60 to 100°C utilizing the exothermic reaction until a resin having the characteristics mentioned is obtained. The reaction is preferably carried out in the presence of oxygen, for example, by passing air through the
10 reaction mixture.

The reaction may be accelerated by the addition of suitable catalysts (such as dibutyl tin dioxide, dibutyl tin dilaurate and triethylamine) in quantities of 0.01 to 2.5% by weight, based on the weight of the reaction mixture as a whole.

15 The reaction product may be protected against premature and unwanted polymerization by the addition of suitable inhibitors and antioxidants each in quantities of 0.001 to 0.3% by weight, based on the mixture as a whole.

Where the residual organic solvent content has to
20 meet particularly stringent requirements, the solvent may be partly removed by distillation before, during and/or after neutralization or dissolution or dispersion of the resin in water. Removal of solvents from the solution or dispersion by distillation is only appropriate for solvents which form an
25 azeotrope with water.

After the urethanization reaction, small quantities of other organic solvents (such as ethanol, n-propanol, isopropanol, n-butanol, tert.-butanol, pentanol, hexanol, octanol, butyl glycol, ethyl glycol, butyl diglycol, ethyl
30 diglycol, methyl diglycol and methoxypropanol) may be added to obtain certain properties.

The reaction products, which preferably accumulate in the form of 60 to 95% by weight solutions in organic solvents, are dissolved or dispersed in the form of these solutions in a
35 mixture of water and ammonia, the ammonia preferably being used

in such a quantity that 45 to 100%, preferably 60 to 100% of the carboxyl groups are neutralized. At the same time, it is important to ensure that the pH value of the solution or dispersion formed is between 6.0 and 8.5, preferably between 6.5 and 8.0. The quantity of water used is gauged so that a solids content within the limits mentioned above is obtained.

The aqueous solutions or dispersions obtained in accordance with the present invention are valuable aqueous binders for coating compositions. They may be used as such or in combination with auxiliaries and additives known from paint technology (such as fillers, pigments, solvents, flow control agents and the like) for the production of coatings on any substrate.

Suitable substrates include paper, paperboard, leather, wood, plastics, nonwovens, textiles, ceramic materials, mineral materials, glass, metal, artificial leather, photographic materials, for example, paper coated with a photographic layer.

The coating compositions may be applied in known manner by spray coating, knife coating, roll coating, spread coating, dip coating or casting. After evaporation of the water and any inert solvents present, the coatings may be crosslinked either by high-energy radiation (such as UV light, electron beams or gamma rays) or by curing with metal salts of siccative acids and (hydro)peroxides or with metal salts of siccative acids or with (hydro)peroxides alone at temperatures of 80 to 250°C. At temperatures above 150°C, it is generally not necessary to add (hydro)peroxides and/or metal salts.

When the coatings are crosslinked by UV irradiation, photoinitiators have to be added to the coating compositions. Suitable photoinitiators include known compounds such as those which are described, for example, in the book by J. Korsar, Light-Sensitive Systems, J. Wiley & Sons, New York-London-Sydney, 1965.

Other suitable photoinitiators include benzoin ethers such as benzoin isopropyl ether, benzil ketals such as benzil dimethyl ketal, and hydroxyalkyl phenones such as 2-hydroxy-2-methyl-1-phenylpropan-1-one. The photoinitiators are used in quantities of 0.1 to 10% by weight, preferably 0.1 to 5% by weight, depending upon the particular application for the compounds according to the invention. The photoinitiators may be used either individually or, by virtue of favorable synergistic effects, in combination with one another.

The siccatives which are optionally used include cobalt, lead or manganese salts of acids such as linseed oil fatty acid, tall oil fatty acids and soybean oil fatty acids; resinic acids such as abietic acid and naphthenic acid; acetic acid; and isooctanoic acid. When they are used, they are used in the form of organic solutions in such quantities that the metal content, based on the weight of the dispersed hydrophilic and hydrophobic polymers, corresponds to between 0.001 and 1% by weight.

Examples of suitable (hydro)peroxides include dicumyl peroxide, di-tert. butyl peroxide, benzoyl peroxide, cyclohexanone peroxide, methyl ethyl ketone peroxide, acetyl acetone peroxide, dinonyl peroxide, bis-(4-tert.-butyl-cyclohexyl)-peroxydicarbonate, tert. butyl hydroperoxide, 2,5-dimethylhexane-2,5-hydroperoxide, diisopropylbenzene monohydroperoxide and hydrogen peroxide. These (hydro)peroxides are preferably used in quantities of 1 to 10% by weight, based on the weight of the dispersed or dissolved oligourethanes.

In the following examples, all parts and percentages are by weight unless otherwise indicated.

EXAMPLES

The quantities of components a) and b) set forth in Table 1 were dissolved in butyl acetate together with 0.2% tin dioctoate and 0.1% 2,6-di-tert. butyl-p-cresol (see Table 1) and the resulting solution was heated to 60°C while air was passed through. The quantity of component c) set forth in

Mo-3552

-10-

Table 1 was then added dropwise. After 1 hour, the temperature was increased to 80°C and the mixture was kept at that temperature until the NCO content had fallen to below 0.1%

5 A solution of ammonia in water was then added to the solution of the oligourethane containing (meth)acryloyl groups obtained in a quantity sufficient to obtain a solids content of 50%. Ammonia was then added to provide a degree of neutralization of 80%, based on dimethylol propionic acid. A solution of ammonia in water was then added in an amount which resulted
10 in an aqueous dispersion or solution having a pH value of approx. 7. The solids contents obtained and the pH values are set forth in Table 1.

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Mo-3552

TABLE 1
Examples

	1	2	3	4	5	6
<u>Weighed portion (%)</u>						
<u>Component a</u>						
Hydroxyethyl acrylate	26.8	7.0				
Hydroxyethyl methacrylate						31.0
Butane-1,4-diol monoacrylate					33.3	
4x-ethoxylated trimethylol propane diacrylate		50.0	63.4	67.6		
<u>Component b</u>						
Dimethylol propionic acid	7.7	10.0	8.5	9.0	15.5	16.0
<u>Component c</u>						
Isophorone diisocyanate		33.0	28.1		51.2	53.0
Toluene-2,4-diisocyanate				23.4		
Trimerized 1,6-diisocyanato- hexane	65.5					
Butylacetate	25.0	11.1	11.1	11.1	11.1	25.0

Mo-3552

TABLE 1 - Continued

	<u>Examples</u>					
	1	2	3	4	5	6
<u>Acid value (mg KOH/g) of</u> <u>the product formed</u>	36	32	33	37	39	34
<u>Solids content of the</u> <u>aqueous dispersion (%)</u>	40	42	45	37	43	46
<u>ph value of the aqueous</u> <u>dispersion</u>	7.0	7.3	7.0	7.5	7.9	7.0

Mo-3552

Application Examplesa) Photochemical curing

5 5% 2-hydroxy-2-methyl-1-phenylpropan-1-one was added to the product of Examples 1, 2, 3 and 4 before the final addition of ammonia water.

 The aqueous dispersions were then applied to a glass plate in a wet film thickness of 60 μm . After evaporation of the water, the film was cured beneath two IST lamps (impulse lamps manufactured by Strahlentechnik Hildebrand, Werner und
10 Pfleiderer, output 80 watts/cm, arranged at a distance from the film of 20 cm) at a processing speed of 14 m/minute.

 Clear, extremely hard (Konig pendulum hardness in accordance with DIN 53 157: approx. 200 secs.) and scratch-resistant coatings which were resistant to water and
15 chemicals were obtained.

 Scratch resistance was determined by the finger nail test while resistance to water and chemicals was tested by the application of cotton wool plugs impregnated with

- water (16 hours)
- 20 - ethanol, 50% (1 hour)
- detergent (1 hour)
- acetone (10 seconds).

b) Thermal curing

 The aqueous dispersions of Examples 2, 3, 5 and 6
25 were applied to a glass plate in a wet film thickness of 60 μm and cured for 30 minutes and 180°C. Clear, hard, scratch-resistant and water-resistant coatings were formed.

 Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be
30 understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

- 14 -

The embodiments of the invention in which exclusive property or privilege is claimed are defined as follows:

1. An aqueous solution or dispersion of oligourethanes having
5 a pH of 6.0 to 8.5 wherein the dissolved or dispersed oligourethanes contain carboxyl groups at least partially neutralized with ammonia and have

- 10 i) a double bond content in the form of (meth)acryloyl groups (expressed as C=C, molecular weight 24) of 3 to 15% by weight and
- ii) a content of carboxyl groups, including the carboxyl groups neutralized with ammonia, which corresponds to an acid value of 20 to 100,

wherein said oligourethanes comprise the reaction product at an NCO:OH
15 equivalent ratio of 0.5:1 to 1:1 of

- a) 20 to 80% by weight of an acryloyl component comprising at least one monohydric alcohol having one or more (meth)acryloyl groups and a molecular weight of 116 to 1000,
- b) 4.5 to 20% by weight of at least one 2,2-bis-(hydroxymethyl)alkane
20 carboxylic acid having at least 5 carbon atoms and
- c) 15 to 75% by weight of at least one polyisocyanate component comprising at least one organic polyisocyanate having a molecular weight of 168 to 1000,

wherein the percentages of a), b) and c) add up to 100.

25 2. The solution or dispersion of Claim 1 wherein 45 to 100% of the carboxyl groups are neutralized with ammonia.

3. The solution or dispersion of Claim 1 wherein said 2,2-bis-(hydroxymethyl)-alkane carboxylic acid comprises 2,2-bis-(hydroxymethyl)-propionic acid.

30 Mo-3552

- 15 -

4. The solution or dispersion of Claim 2 wherein said 2,2-bis-(hydroxymethyl)-alkane carboxylic acid comprises 2,2-bis-(hydroxymethyl)-propionic acid.

5. A process for the production of an aqueous solution or
5 dispersion of oligourethanes which comprises reacting
- a) 20 to 80% by weight of an alcohol component comprising at least one monohydric alcohol having one or more (meth)acryloyl groups and a molecular weight of 116 to 1,000,
 - b) 4.5 to 20% by weight of at least one 2,2-bis-(hydroxymethyl)-
10 alkane carboxylic acid having at least 5 carbon atoms and
 - c) 15 to 75% by weight of at least one polyisocyanate component comprising at least one organic polyisocyanate having a molecular weight of 168 to 1,000,
- by initially introducing components a) and b), then reacting these
15 components with component c) at a temperature of 50 to 100°C until the reaction mixture contains no more free isocyanate groups and subsequently dissolving or dispersing the reaction mixture in water, the carboxyl groups being at least partly neutralized by addition of ammonia during the dissolving or dispersing step so that the resulting solution or
20 dispersion has a pH value of 6.0 to 8.5, provided that
- A) the percentages of a), b) and c) add up to 100,
 - B) the amounts of a), b) and c) correspond to an NCO:OH equivalent ratio of 0.5:1 to 1:1 and
 - C) the amounts of a), b) and c) are otherwise selected within the
25 stated limits so that the resulting oligourethanes have
- i) a double bond content in the form of (meth)acryloyl groups (expressed as C=C, molecular weight 24) of 3 to 15% by weight and

Mo-3552

- 16 -

- ii) a content of carboxyl groups, including the carboxyl groups neutralized with ammonia, which corresponds to an acid value for the oligourethanes of 20 to 100.
- 6. A coated substrate wherein the coating is prepared from a
- 5 coating composition comprising the aqueous solution or dispersion of oligourethanes of Claim 1.

Mo-3552



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 87 20 1766

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 055 477 (ASAHI) * Claims; page 13, line 9 * -----	1-3, 5- 18, 22- 24	C 09 D 3/48
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 09 D 3/48
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-12-1987	Examiner FOUQUIER J.P.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			